

Crystal and molecular structure of 3-(2-amino-pyridinium)-propionate monohydrate

Mirosław Szafran ^{*}, Iwona Kowalczyk, Andrzej Katrusiak

Faculty of Chemistry, Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań, Poland

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Abstract

A novel betaine derivative, 3-(2-amino-pyridinium)-propionate monohydrate, has been synthesized and its structure studied by X-ray diffraction, FTIR, Raman, ¹H and ¹³C NMR spectroscopies and by DFT calculations. The crystals are monoclinic, space group $P2_1/c$ with $a=8.0800(16)$, $b=15.242(3)$, $c=7.1698(14)$ Å, $\beta=104.30(3)^\circ$ and $Z=4$. Each oxygen atom of the carboxylate group is engaged in two intermolecular hydrogen bonds, one with water molecule and the other with amine group. The water molecules link the molecules of 3-(2-amino-pyridinium)-propionate into planar zigzag chains along the b axis. The screening constants for ¹H and ¹³C atoms have been calculated by GIAO/B3LYP/6-31 G(d,p) and analyzed. Linear correlations between the experimental ¹H and ¹³C chemical shifts and the computed screening constants have been obtained. Raman and FTIR spectra of the title betaine have been investigated.

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1. Introduction

In zwitterionic molecules, $R_3X^+-(CH_2)_n-YO_{(2-4)}^-$, oppositely charged quaternary ammonium ($X=N$), quaternary phosphonium ($X=P$) or tertiary sulfonium ($X=S$) groups are connected with the necked carboxylate group ($Y=COO$) via methylene groups ($n=1-10$). The above compounds are known as betaines ($R_3N^+-(CH_2)_n-COO^-$), phosphonium betaines ($R_3P^+-(CH_2)_n-COO^-$), or sulfonium betaines ($R_2S^+-(CH_2)_n-COO^-$) [1]. When the carboxylate group is replaced by sulfato or sulfito groups than sulfobetaines ($R_3N^+-(CH_2)_n-SO_2O^-$), sulfitobetaines ($R_3N^+-(CH_2)_n-OSO_2^-$), sulfatobetaines ($R_3N^+-(CH_2)_n-OSO_3^-$), and phosphinatebetaines ($R_3P^+-(CH_2)_n-SO_2O^-$) are formed [1]. Replacement of the carboxy or sulfonic groups by a phosphinate or phosphonate group led to phosphinatebetaines ($R_3N^+-(CH_2)_n-P=O(R)O^-$), phosphonatebetaine ($R_3N^+-(CH_2)_n-P=O(OR)O^-$), phosphitobetaines ($R_3N^+-(CH_2)_n-O-P=O(H)O^-$), and phosphatobetaines ($R_3N^+-(CH_2)_n-OP=O(OH)O^-$) [1]. Another group of betaines is heterocyclic betaines and their salts, in

which the carboxylate group in pyridine betaines is replaced by azolyl or benzoimidazolyl-2 [2].

Relatively large group are pyridine betaines which are good proton acceptors. Structures of several pyridine betaines and their 1:1 and 2:1 complexes with HCl, HBr, $HClO_4$, H_2SO_4 , HSO_3F , $C_6H_5-CH_2-COOH$, C_6Cl_5OH and $2,6-Cl_2-4-NO_2-C_6H_2-OH$ have been determined by X-ray diffraction [3–25].

An interesting examples of betaines are pyridinium betaines of squaric acid, in which one oxygen atom of dianion of squaric acid is replaced by R-pyridinium ring [26,27].

In previous studies we have analyzed conformation of 2-aminopyridinium-acetate (2-aminopyridinium betaine; IUPAC name, 1-carboxymethyl-2-amino-pyridinium inner salt) and its monohydrate, $2-NH_2-C_5H_4N^+CH_2-COO^- \cdot H_2O$ [28]. In this work, we report synthesis, crystal structure, FTIR and Raman spectra and some DFT results of 3-(2-amino-pyridinium)propionate monohydrate (monohydrate of 1-carboxyethyl-2-amino-pyridinium inner salt), $2-NH_2-C_5H_4N^+CH_2-CH_2-COO^- \cdot H_2O$.

2. Experimental

2.1. Synthesis

$2-NH_2$ -pyridine (0.1 m) and 3-bromo-propionic acid (0.1 m) were stirred for 30 h at room temperature up

* Corresponding author. Tel.: +48 61 8291320; fax: +48 61 8658008.
E-mail address: szafran@amu.edu.pl (M. Szafran).

to solidification and then left to stand for 2 days. The crude 3-(2-amino-pyridinium)propionic acid bromide was recrystallized from acetonitrile, m.p. 250–252 °C, yield 84%.

3-(2-Amino-pyridinium)propionic acid bromide (1 equiv) was dissolved in water and propylene oxide (1.3 equiv) dissolved in methanol was added slowly. After 4 days the reaction mixture was extracted with ether and the residue was evaporated under reduced pressure to dryness. The raw 3-(2-amino-pyridinium)-propionate monohydrate, 2-NH₂PB₂·H₂O was recrystallized from methanol, m.p. 124–126 °C, yield 63%.

Deuterated compound was obtained by dissolving the sample in D₂O (twice), evaporating to dryness and recrystallization from a CH₃OD.

2.2. Instrumentation

The X-ray diffraction measurements were carried out using a KUMA KM-4 CCD diffractometer. The structure was solved by direct methods with SHELXS-97 [29] and refined by the full-matrix least squares method on F^2 data using SHELXL-97 [30]. The crystal data and details concerning the data collection and structure refinement are given in Table 1. Atomic coordinates and equivalent displacement parameters are listed in Table 2. The parameters in the CIF form are available as Electronic Supplementary Information from Cambridge

Table 1

Crystal data and structure refinement for 3-(2-amino-pyridinium)-propionate monohydrate

Empirical formula	C ₈ H ₁₀ N ₂ O ₂
Formula weight	166.18
Temperature (K)	293(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	
<i>a</i> (Å)	8.0800(16)
<i>b</i> (Å)	15.242(3)
<i>c</i> (Å)	7.1698(14)
β (deg)	104.30(3)
Volume (Å ³)	855.7(3)
<i>Z</i>	4
Calculated density (g/cm ³)	1.290
Absorption coefficient (mm ⁻¹)	0.095
<i>F</i> (000)	352
Crystal size (mm)	0.5×0.3×0.2
θ range for data collection (deg)	3.22–29.41
Index range	$-10 \leq h \leq 10$ $-20 \leq k \leq 20$ $-5 \leq l \leq 9$
Reflections collected/unique	6219/2172
<i>R</i> (int)	0.0355
Completeness to θ_{\max}	$\theta = 29.90$, 90.9%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2172/0/135
Goodness-of-fit on F^2	1.262
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0354$, $wR_2 = 0.1000$
<i>R</i> indices (all data)	$R_1 = 0.0538$, $wR_2 = 0.1229$
Largest diff. peak and hole (e Å ⁻³)	0.287 and -0.277

Table 2

Atomic coordinates and equivalent isotropic displacement parameters (Å²) for 3-(2-amino-pyridinium)-propionate monohydrate

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
N(1)	0.8148(2)	0.16828(9)	0.2403(2)	0.0285(4)
C(2)	0.7079(2)	0.23829(11)	0.1972(3)	0.0265(4)
N(2)	0.5469(2)	0.22916(11)	0.1041(3)	0.0377(5)
C(3)	0.7765(3)	0.32212(12)	0.2568(3)	0.0313(4)
C(4)	0.9414(3)	0.33151(13)	0.3497(3)	0.0379(5)
C(5)	1.0473(3)	0.25813(15)	0.3930(3)	0.0414(5)
C(6)	0.9812(3)	0.17841(14)	0.3379(3)	0.0366(5)
C(7)	0.7588(3)	0.07767(12)	0.1840(3)	0.0352(5)
C(8)	0.7113(3)	0.03003(13)	0.3457(3)	0.0373(5)
C(9)	0.6542(2)	-0.06467(12)	0.2971(3)	0.0305(4)
O(1)	0.6314(2)	-0.08960(10)	0.12739(19)	0.0396(4)
O(2)	0.62942(19)	-0.10904(9)	0.4334(2)	0.0403(4)
O(1w)	0.2381(2)	0.03831(12)	0.1966(3)	0.0499(5)
H(1w)	0.298(4)	0.05411(19)	0.324(4)	0.060
H(2w)	0.291(4)	0.047(2)	0.123(4)	0.060
H(21)	0.5043	0.1839	0.0408	0.046(7)
H(22)	0.4981	0.2679	0.1031	0.067(10)
H(3)	0.7063	0.3713	0.2314	0.057(8)
H(4)	0.9853	0.3871	0.3854	0.044(6)
H(5)	1.162(4)	0.2616(19)	0.449(4)	0.054(7)
H(6)	1.0507	0.1291	0.3672	0.052(7)
H(71)	0.8502	0.0464	0.1468	0.059(8)
H(72)	0.6611	0.0793	0.0736	0.051(7)
H(81)	0.6197	0.0617	0.3815	0.045
H(82)	0.8089	0.0299	0.4563	0.045

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Crystallographic Data-base Centre (CCDC reference number 283154).

The calculations were performed using the Gaussian 98 package [31] at the B3LYP [32,33] levels of theory with the 6-31G(d,p) basis set [34].

NMR spectra were measured with a Varian Gemini 300 VT spectrometer, operating at 300.07 and 75.4614 MHz for ¹H and ¹³C, respectively. Typical conditions for the proton spectra were pulse width 32°, acquisition time 5 s, FT size 32 K and digital resolution 0.3 Hz per point, and for the carbon spectra pulse width 60°, FT size 60 K and digital resolution 0.6 Hz per point; the number of scans varied from 1200 to 10,000 per spectrum. ¹³C and ¹H chemical shifts, measured in D₂O

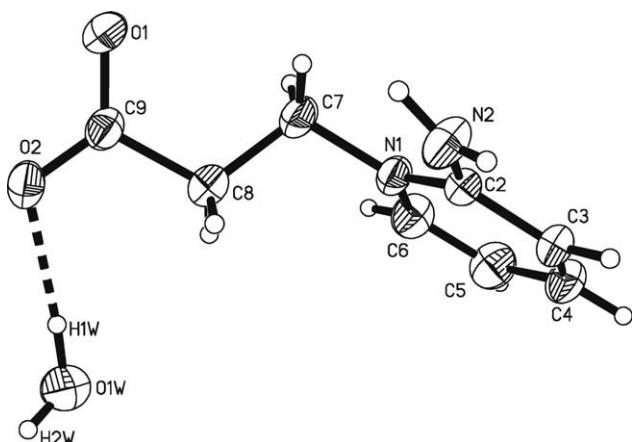


Fig. 1. ORTEP drawing (at 50% probability level) of 3-(2-amino-pyridinium)-propionate monohydrate with atom numbering.

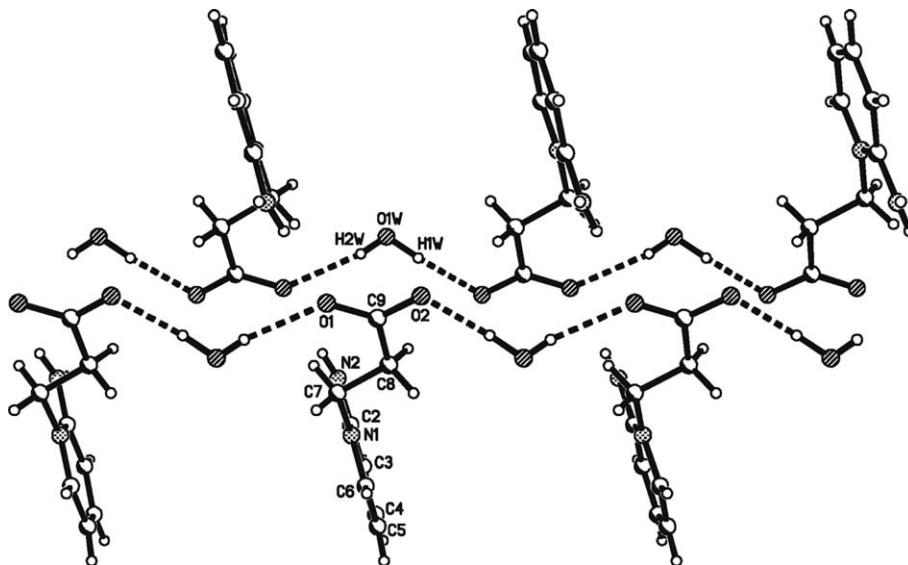


Fig. 2. Auto-stereogram of two neighboring hydrogen bonded chains of 3-(2-amino-pyridinium)-propionate monohydrate and water molecules. Hydrogen bonds are denoted by the dashed lines.

relative to internal dioxane, were 67.35 and 3.55 ppm, respectively. The FTIR spectra in Nujol and Fluorolube emulsions were measured at 2 cm^{-1} resolution using a Bruker IFS 113v spectrometer, which was evacuated to avoid water and CO_2 absorption. Raman spectrum was recorded on a Magna 760 Nicolet operating at the 1064 nm exciting line of a Nd:YAG laser.

3. Results and discussion

3.1. Molecular parameters

Molecular structure of 3-(2-amino-pyridinium)-propionate monohydrate and the numbering scheme are shown in Figs. 1–3, respectively. The functional atomic coordinates with equivalent thermal parameters, bond lengths and bond angles are listed in Tables 2 and 3, respectively. Each water molecule links two adjacent betaines via two slightly different hydrogen bonds of lengths 2.818 and 2.886 Å into a planar zigzag chains along b axis (Figs. 2 and 3). The NH_2 group is engaged in two hydrogen bonds of the lengths 2.859 and 2.828 Å with the COO groups of neighboring betaines. The angle between the planes through the pyridine ring and COO group is $76.27(9)^\circ$. In 2-aminopyridine acetate the hydrogen bonds between the NH_2 and COO^- groups are slightly longer (Table 4). As shown in Table 3 the $\text{C}-\text{O}$ bond lengths in the betaine investigated are similar, while in 2-aminopyridine acetate these bonds lengths are much different [24].

The bond length between NH_2 and the pyridine ring is equal 1.315(3) Å. Slightly longer distances are in 2-aminopyridine acetate monohydrate (1.329(2) Å) [24] and its hydrochloride (1.330(3) Å) [25]. These values are close to the average of single $\text{C}-\text{N}$ (1.46 Å) and double $\text{C}=\text{N}$ (1.15 Å) bonds. In 2-amino-4-methyl-pyridine the $\text{C}-\text{NH}_2$ distance is 1.363 Å [35] and becomes shorter (1.329 Å) on protonation [36]. These

data indicate that in both 2-amino-pyridine betaines the NH_2 group appears between amino and imino tautomers ($\text{C}-\text{NH}_2 \leftrightarrow \text{C}=\text{NH}$).

3.2. FTIR and Raman spectra

The FTIR and Raman spectra of the investigated betaine are shown in Fig. 4. The intense broad absorption in the 3500–2600 cm^{-1} region corresponds to the overlapping νOH and νNH vibrations of water molecule and NH_2 group. On deuteration this absorption shifts to lower wavenumbers and

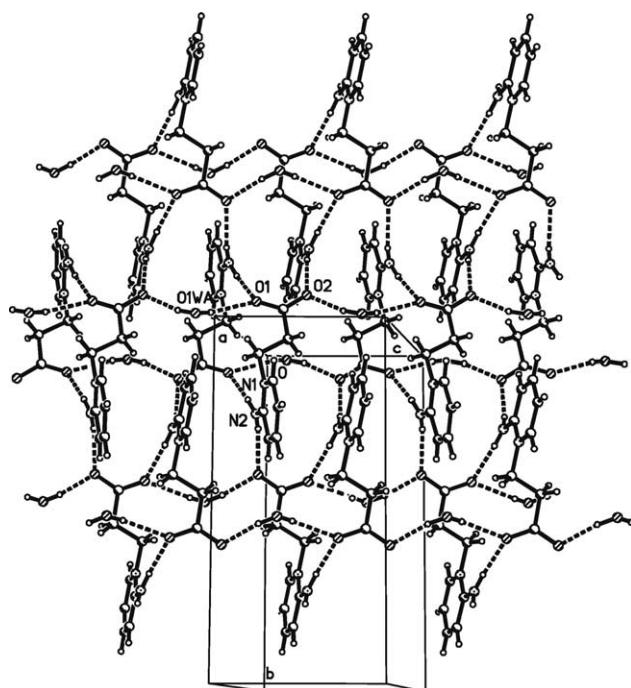


Fig. 3. Auto-stereogram of the crystal packing of 3-(2-amino-pyridinium)-propionate monohydrate. Hydrogen bonds are denoted by the dashed lines.

Table 3

X-Ray and calculated bond lengths (\AA) and bond angles (deg) for 3-(2-amino-pyridinium)-propionate monohydrate

Bond length (\AA)	Bond angle (°)		Torsion angle (°)
N(1)–C(2)	1.360(2)	N(1)–C(2)–C(3)	117.42(17)
N(1)–C(6)	1.362(2)	N(1)–C(6)–C(5)	121.51(19)
N(1)–C(7)	1.478(2)	N(1)–C(7)–C(8)	111.20(16)
N(2)–C(2)	1.315(3)	N(2)–C(2)–N(1)	121.71(16)
C(2)–C(3)	1.416(2)	N(2)–C(2)–C(3)	120.87(17)
C(3)–C(4)	1.342(3)	C(2)–N(1)–C(6)	121.24(16)
C(4)–C(5)	1.396(3)	C(2)–N(1)–C(7)	122.46(16)
C(5)–C(6)	1.347(3)	C(7)–N(1)–C(6)	116.30(16)
C(7)–C(8)	1.496(3)	C(2)–C(3)–C(4)	120.83(18)
C(8)–C(9)	1.529(3)	C(3)–C(4)–C(5)	120.26(18)
C(9)–O(1)	1.244(2)	C(4)–C(5)–C(6)	118.7(2)
C(9)–O(2)	1.245(2)	C(7)–C(8)–C(9)	113.72(16)
		O(1)–C(9)–O(2)	126.03(18)
		O(1)–C(9)–C(8)	118.34(17)
		O(2)–C(9)–C(8)	115.58(16)
		C(6)–N(1)–C(7)–C(8)	83.5(2)
		N(1)–C(7)–C(8)–C(9)	−179.28(16)
		C(7)–C(8)–C(9)–O(1)	−8.9(3)
		C(7)–C(8)–C(9)–O(2)	173.40(18)

Table 4

Geometry of hydrogen bonds in 3-(2-amino-pyridinium)-propionate and 2-amino-pyridinium-acetate monohydrates

D–H···A	D···A	D–H	H···A	<DHA	Symmetry code	ν_{ND}	ν_{OD}
$2\text{-NH}_2\text{C}_5\text{H}_4\text{N}^+\text{CH}_2\text{CH}_2\text{COO}^- \cdot \text{H}_2\text{O}$							
N(2)–H(21)···O(1)	2.859(2)	0.85	2.02	170.3(3)	$1-x, -y, -z$	2405	
N(2)–H(22)···O(2)	2.828(2)	0.71	2.13	171.1(3)	$1-x, -0.5+y, 0.5-z$	2223	
O(1w)–H(1w)···O(2)	2.818(2)	0.95	1.89	164.3(3)	x, y, z		2467
O(1w)–H(2w)···O(1)	2.886(2)	0.77	2.14	163.0(3)	$x, y, 1-z$		2603
$2\text{-NH}_2\text{C}_5\text{H}_4\text{N}^+\text{CH}_2\text{COO}^- \cdot \text{H}_2\text{O}$ [24]							
N(2)–H(21)···O(1)	2.967	0.999	1.976	171.3	$0.5-x, -0.5+y, z$	2482	
N(2)–H(22)···O(2)	2.866	0.850	0.850	168.4	$-x, 1-y, -z$	2397	
O(1w)–H(1w)···O(1)	2.795	0.861	0.861	176.2	x, y, z		2413
O(1w)–H(2w)···O(1w)	2.828	0.788	0.788	172.4	$-0.5+x, y, 0.5-z$		2585

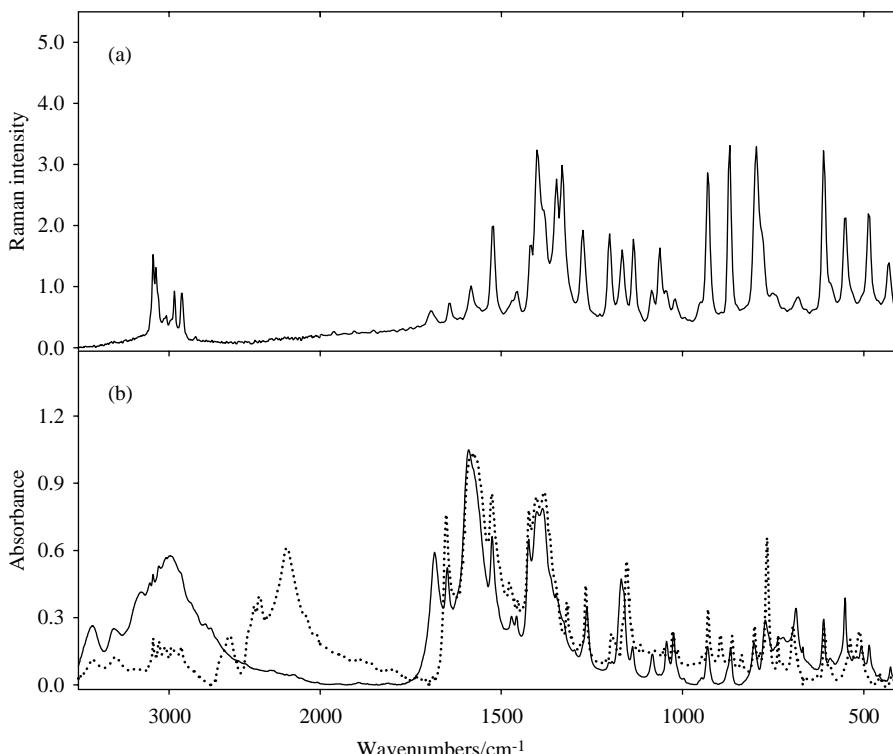
Fig. 4. Spectra of 3-(2-amino-pyridinium)-propionate monohydrate: (a) Raman spectrum in the solid state; and (b) FTIR spectrum in Nujol and Fluorolube emulsions; dotted line denotes spectrum of deuterated molecule (2-ND₂-C₅H₄N⁺-CH₂CH₂COO⁻ · D₂O).

Table 5

Tentative assignments of the observed absorption bands in the Raman and FTIR spectra of 3-(2-amino-pyridinium)-propionate monohydrate, and its deuterium analogue

2-NH ₂ PB2·H ₂ O		Assignment	2-ND ₂ PB2·D ₂ O	Assignment
Raman	IR		IR	
	3500–2600	$\nu\text{H}_2\text{O} + \nu\text{NH}_2$	2603 2437 2405 2223	$\nu\text{D}_2\text{O}$ $\nu\text{D}_2\text{O}$ νND_2 νND_2
3106		νCH	3105	νCH
3088		νCH	3067	νCH
3019		νCH	3028	νCH
2964		νCH_2	2988	νCH_2
2916		νCH_2	2918	νCH_2
1694	1684	δNH_2	1319	δND_2
1643	1648	$\nu_{\text{as}}\text{COO}$	1652	$\nu_{\text{as}}\text{COO}$
1584	1590	$\nu\text{-Ring}$	1582	$\nu\text{-Ring}$
1523	1524	$\nu\text{-Ring}$	1526	$\nu\text{-Ring}$
	1470	$\nu\text{-Ring}$	1477	$\nu\text{-Ring}$
1457	1458	βCH_2	1454	βCH_2
1419	1424	$\nu\text{-Ring}$	1423	$\nu\text{-Ring}$
1401	1402	$\nu\text{-Ring}$	1403	$\nu\text{-Ring}$
1348	1386	$\nu_{\text{s}}\text{COO}$	1382	$\nu_{\text{s}}\text{COO}$
1332			1318	βCH
1275	1263	βCH	1267	βCH
1228		βCH		
1210	1194	βCH	1196	βCH
1167	1169	βNH_2	895	βND_2
1135	1138	βCH	1154	βCH
1085	1083	βCH	1116	βCH
1063		βCH	1052	βCH
1046	1044	βCH	1027	βCH
1021	1024	βCH	1013	βCH
930	931	γCH	929	νCC
871	867	γCH	862	γCH
797	803	γCH	801	γCH
751	772	γCH	767	γCH
682	687	γOHO	512	γODO
611	610	$\gamma\text{-Ring}$	609	$\beta\text{-Ring}$
551	552	$\gamma\text{-Ring}$	537	$\gamma\text{-Ring}$
	507	$\gamma\text{-Ring}$		
486	485	$\gamma\text{-Ring}$	456	$\gamma\text{-Ring}$
431	426	$\gamma\text{-Ring}$	425	$\gamma\text{-Ring}$

The abbreviations are: ν , stretching; β , in-plane-bending; γ , out-of-plane-bending modes.

four bands at 2603, 2467, 2405 and 2223 cm⁻¹ are distinguished. The first two bands belong to D₂O molecule, but the last two to the ND₂ group.

In the betaine investigated the NH₂ groups are engaged in shorter hydrogen bonds but water molecule in longer ones in comparison to those in 2-amino-pyridinium acetate monohydrate (Table 4). The differences between νND and νOD bands in the two betaines agree well with the differences in their hydrogen bonds.

An interesting point is the difference between the $\nu_{\text{as}}\text{NH}_2$ and $\nu_{\text{s}}\text{NH}_2$ vibrations in amines. A typical difference between these frequencies is $\Delta\nu=65–130\text{ cm}^{-1}$ [37–39]. The larger difference ($\Delta\nu=182\text{ cm}^{-1}$) in the betaine investigated agrees well with the presence of two different hydrogen bonds (Table 4).

The $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ are located at 1648 and 1386 cm⁻¹ and are at slightly higher wavenumbers than in pyridine betaine [40] and betaines [39–42]. The band at 1684 cm⁻¹, which shifts on deuteration to 1319 cm⁻¹ corresponds to βNH_2 vibration. In 2-aminopyridine this band is at 1650 cm⁻¹ in liquid but at 1635 cm⁻¹ in vapour [40]. The βNH_2 band is at 1169 cm⁻¹ and on deuteration it is shifted to 895 cm⁻¹. Probable assignments of the bands observed are listed in Table 5.

3.3. ^1H and ^{13}C NMR

The proton chemical shift assignments (Table 6) are based on the 2D COSY experiments, in which the proton–proton connectivity is observed through the off-diagonal peaks in the counter plot. The 2D heteronuclear shifts correlated counter map (HETCOR) has been used to identify resonances in the ^{13}C NMR spectra.

The relations between the experimental ^1H and ^{13}C chemical shifts (δ_{exp}) and the GIAO (gauge including atomic orbitals) screening tensors (σ_{calc}), which are now widely used in efficient implementation [43–45], are usually linear and described by the following equation: $\delta_{\text{exp}}=a+b*\sigma_{\text{calc}}$. The differences in ^1H and ^{13}C chemical shifts between unsubstituted pyridine betaines [46] and their 2NH₂-derivatives (Ref. [26] and Table 6) follow the additive rules for NH₂ substituent [37].

3.4. B3LYP calculations

Seven isolated entities, denoted as 2–8, were optimized at the B3LYP/6-31G(d,p) level of theory and their structures are shown in Fig. 5. These structures differ in the type of hydrogen bonds. In all optimized structures one proton of the amine group is transferred to the carboxylate group and the intramolecular HN···HO hydrogen bond of lengths between

Table 6

Chemical shifts (δ , ppm) in D₂O and calculated GIAO nuclear magnetic shielding tensors (σ_{cal}) for 3-(2-amino-pyridinium)-propionate monohydrate

	δ_{exp}	δ_{pred}	σ_{calc}	Δ
C(6)	143.4	143.6	57.64	9.2
C(5)	115.9	105.6	91.90	-14.4
C(4)	140.4	139.5	61.29	5.4
C(3)	114.5	122.0	77.09	-13.0
C(2)	154.7	163.4	39.82	-2.1
C(7)	51.9	52.9	139.50	
C(8)	35.8	36.8	154.06	
H(6)	7.65	7.91	24.71	-1.09
H(5)	6.69	6.73	26.00	-1.19
H(4)	7.60	7.60	24.98	-0.74
H(3)	6.83	6.42	25.73	-1.05
H(7)	4.18	4.23	27.92	
H(8)	2.54	2.61	29.35	

The predicted GIAO chemical shifts were computed from the linear equation $\delta_{\text{exp}}=a+b\sigma_{\text{calc}}$ with a and b determined from the fit of the experimental data. Δ (ppm) is effect of NH₂ on chemical shifts on betaine. $a_{\text{C}}=207.4382$; $b_{\text{C}}=-1.1076$; $r^2=0.9831$, $a_{\text{H}}=36.1495$; $b_{\text{H}}=-1.1432$; $r^2=0.9933$.

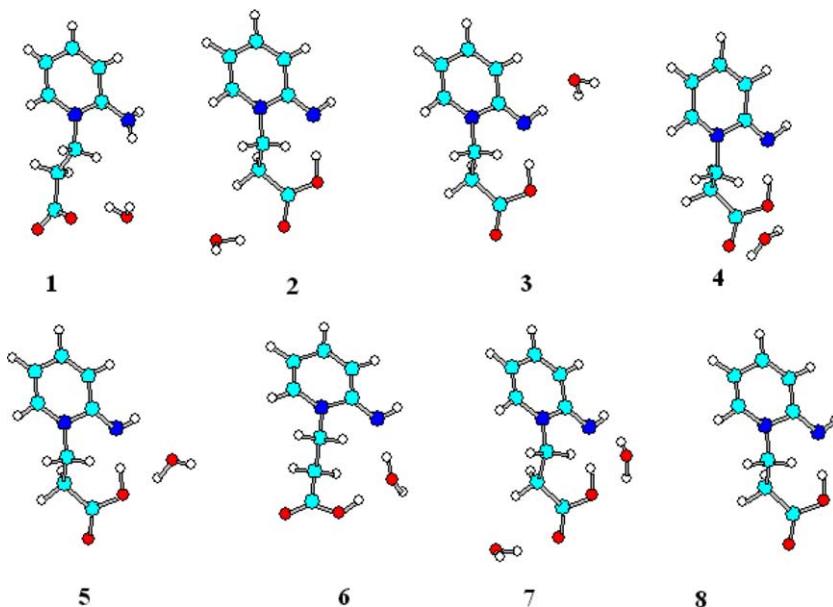


Fig. 5. Comparison of the X-ray (1) and B3LYP/6-31G(d,p) (2–8) most stable structures: $2\text{-NH}_2\text{-C}_5\text{H}_4\text{N}^+\text{-CH}_2\text{CH}_2\text{COO}^- \cdot \text{H}_2\text{O}$ (1–6), $2\text{-NH}_2\text{-C}_5\text{H}_4\text{N}^+\text{-CH}_2\text{CH}_2\text{COO}^- \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}$ (7) and $2\text{-NH}_2\text{-C}_5\text{H}_4\text{N}^+\text{-CH}_2\text{CH}_2\text{COO}^-$ (8).

Table 7

Selected X-ray and DFT parameters of 3-(2-amino-pyridinium)-propionate monohydrate, $2\text{-NH}_2\text{-C}_5\text{H}_4\text{N}^+\text{CH}_2\text{-CH}_2\text{-COO}^- \cdot \text{H}_2\text{O}$

X-Ray	B3LYP/6-31G(d,p)							
	1	2	3	4	5	6	7 ^a	8
E (Hartree)		-647.281384	-647.274953	-647.279402	-647.276627	-647.285245	-723.715330	-570.844616
E_{rel} (kcal/mol)	2.42	6.46	3.67	5.41	0			
μ (Debye)	7.935	6.891	7.608	7.407	7.741	7.695	8.217	
N(2)–C(2)	1.315	1.305	1.302	1.306	1.300	1.305	1.314	1.304
N(2)–H	0.851, 0.709	1.017	1.021	1.017	1.017	1.018	1.017	1.017
$\angle \text{C}(2)\text{-N}(2)\text{-H}$	25.2, 113.3	110.9	110.1	110.6	114.4	109.4	110.3	110.7
N(2)···O(1)	2.652	2.666	2.644	2.580			2.652	2.700
$\angle \text{N}(2)\cdots\text{H}\text{-O}(1)$	176.8	176.9	177.2	174.1			176.9	176.1
O(2)–C(9)–O(1)	126.0	121.7	122.9	122.2	123.1	122.2	121.3	122.8
O(2)–C(9)–O(1)–H	174.8	176.0	–176.5	175.7	177.2	176.6	176.0	
HOH···O(1)	2.818	2.828		2.944	2.953		3.032	
$\angle \text{HOH}\cdots\text{O}(1)$	164.3			130.2	144.5		124.9	
HOH···O(2)	2.886	2.828		3.139			2.841	
$\angle \text{HOH}\cdots\text{O}(2)$	162.9	161.5		124.2			160.5	
H–N(2)···HOH						2.731	3.091	
$\angle \text{H-N}(2)\cdots\text{HOH}$						177.4	149.8	
O(1)···OH ₂						2.657		
O(1)H···OH ₂						179.5		
C(10)–O(1)	1.244	1.322	1.333	1.335	1.336	1.335	1.330	1.334
C(10)–O(2)	1.245	1.222	1.213	1.215	1.212	1.212	1.220	1.212
N(1)···O(1)	4.208	3.792	3.807	3.812	3.775	4.463	3.782	3.826
N(1)···O(2)	4.801	4.799	4.793	4.753	4.801	4.618	4.789	4.796
N(1)···OH ₂	4.387	5.532	5.117	4.586	5.268	4.097	3.963/5.526	
N(2)···OH ₂	5.112	6.337	3.125	4.375	3.041	2.731	3.091	
Av. N(1,2)···O(1,2)OH ₂	4.627	5.115	4.211	4.508	4.221	3.977		
$\angle \text{N}(2)\text{H}\cdots\text{OH}_2$			175.4					
N(1)–C(7)–C(8)–C(9)	–179.3	123.8	126.2	126.7	122.0	–176.8	122.6	127.7
C(7)–C(8)–C(9)–O(1)	–8.9	–49.7	–52.9	–60.9	–44.8	–74.3	–52.5	–53.5
C(7)–C(8)–C(9)–O(2)	173.4	130.7	127.4	117.4	132.2	103.3	128.0	126.7
N(2)–C(2)–N(1)–C(6)	–179.6	–178.3	–178.5	–178.3	–179.7	–178.0	–179.1	–178.4
N(2)–C(2)–N(1)–C(7)	0.8	1.5	1.6	2.7	–0.4	0.8	0.3	1.7
O(1)–C(9)–O(2)···HOH		178.3		72.9			180.0	
O(2)–C(9)–O(1)···HOH				93.3	81.4		–93.7	

^a Dihydrate, $2\text{-NH}_2\text{-C}_5\text{H}_4\text{N}^+\text{CH}_2\text{-CH}_2\text{-COO}^- \cdot 2\text{H}_2\text{O}$.

Table 8

Conformations of the $\text{N}^+\text{CH}_2\text{CH}_2\text{COO}(\text{H})$ moiety in betaines and complexes determined by X-ray diffraction

Compound	$\omega(1)$	$\omega(2)$	$\omega(3)$	$\omega(4)$	$\text{N}^+\cdots\text{O}(1)$	$\text{N}^+\cdots\text{O}(2)$	Ref.
2-NH ₂ -C ₅ H ₄ N ⁺ CH ₂ CH ₂ COO ⁻ ·H ₂ O	−179.3(2)	−8.9(3)	173.4(2)		4.208	4.801	
2-Br-C ₅ H ₄ N ⁺ CH ₂ CH ₂ COOH·Br (C ₅ H ₅ N ⁺ CH ₂ CH ₂ COO) ₂ ·Br	179.9(6)	170.3(6)	−11.8(11)	2.5	4.761	4.273	[19]
	−63.0	166.1	−13.9	−2.8	3.045	4.202	[15]
	−74.4	165.4	−16.1	0.3	4.108	3.279	
(C ₅ H ₅ N ⁺ CH ₂ CH ₂ COOH) ₂ SO ₄ ²⁻	68.0(3)	179.8(3)	1.0	9.7	4.280	3.076	[17]
	−66.3(3)	−175.8(3)	4.0	6.2	4.302	3.017	
C ₅ H ₅ N ⁺ CH ₂ CH ₂ COOH·Cl	63.1	−97.1	80.4	2.4	3.193	3.757	[19]
2-(HOCH ₂)-C ₅ H ₄ N ⁺ CH ₂ CH ₂ COOH·Br	−159.3(3)	172.7(3)	−6.6(5)	47	4.791(4)	4.224(4)	[20]
2-(HOCH ₂ CH ₂)-C ₅ H ₄ N ⁺ CH ₂ CH ₂ COOH·Br	179.5(2)	179.5(3)	−1.6(5)	7	4.828(4)	4.213(4)	[20]
[(C ₅ H ₅ N ⁺ CH ₂ CH ₂ COO) ₂ ·Ag ₂] _n [(ClO ₄) _{2n}	78.9(4)	−175.2(3)	8.3(4)		4.493	3.312	[47]
[(C ₅ H ₅ N ⁺ CH ₂ CH ₂ COO) ₂ ·Ag ₂ (NO ₃) ₂] _n	77.6(6)	−179.5(5)	3.6(7)		4.363	3.210	[47]
[(Me ₃ N ⁺ CH ₂ CH ₂ COO) ₂ Ag ₂ ·H ₂ O][ClO ₄] ₂	−169.9	173.6	−6.9		4.858	4.216	[47]
	170.8	60.1	−120.1		4.647	4.351	
Me ₃ N ⁺ CH ₂ CH ₂ COOH·H ₂ O·Br	180.0	−0.0	180.0	−0.0	4.191	4.900	[48]

Torsion angles: $\omega(1)=\text{N}^+-\text{C}(7)-\text{C}(8)-\text{C}(9)$; $\omega(2)=\text{C}(7)-\text{C}(8)-\text{C}(9)-\text{O}(1)$; $\omega(3)=\text{C}(7)-\text{C}(8)-\text{C}(9)-\text{O}(2)$; $\omega(4)=\text{O}(2)-\text{C}(9)-\text{O}(1)-\text{H}$.

2.580–2.700 Å is present in 2–5 and 7–8 (Table 7). Differences between 1 and 2–8 occur also in the N(1)–C(7)–C(8)–C(9) and C(7)–C(8)–C(9)–O(1/2) dihedral angles. In 2–5 and 7–8 the conformation of N(1)–C(7)–C(8)–C(9) units is anticlinal. In crystals, as the data in Table 8 show, the conformation of N(1)–C(7)–C(8)–C(9) units in some betaines is antiperiplanar (trans) but synclinal (gauche) in others. In 6 the water molecule is engaged in two hydrogen bonds, one as a proton acceptor with the COOH group ($\text{O}=\text{C}-\text{O}-\text{H}\cdots\text{OH}_2$, 2.657 Å) and the other as a proton donor with the NH group ($\text{H}-\text{O}-\text{H}\cdots\text{N}-\text{H}$, 2.731 Å). Conformer 6 has the lowest energy, which is probably caused by electrostatic interactions between the positively charged N⁺(1) and N⁺(2) with oxygens of COO[−] group and water molecule; the average distance of these attractive interactions is the shortest in 6 and equal 3.977 Å (Table 7).

4. Conclusions

In the crystal structure of 3-(2-amino-pyridinium)-propionate monohydrate determined by X-ray diffraction, water molecules link two molecules of betaine via two slightly different O(w)H···O–C hydrogen bonds of the lengths 2.818 and 2.886 Å into planar zigzag chains along the *b* axis. The NH₂ group forms additional two hydrogen bonds also with COO groups of neighboring molecules of the lengths 2.859 and 2.828 Å. Five conformers of 3-(2-amino-pyridinium)-propionate monohydrate (2–6), one dihydrate (7) and one anhydrous (8) were optimized by the B3LYP/6-31G(d,p) level of theory. In the optimized molecules 2–5 and 7–8 the intramolecular bond N···H–O–C=O of lengths between 2.580 and 2.700 Å is present, as a result of proton transfer from the N(2)H₂ group to the COO[−] group. In 6 the water molecule joins the COOH and NH groups into a circle. Conformer 6 has the lower energy, which is probably a result of electrostatic interactions between the positively charged N⁺(1) and N⁺(2) atoms with three oxygens (two of COO[−] group and one of water molecule); the average distance of these attractive interactions for 6 is the shortest one and equals 3.977 Å.

The FTIR spectrum of the investigated betaine has been analyzed and found in good agreement with the crystal structure. Good correlations between the experimental ¹³C and ¹H chemical shifts in D₂O solution of 3-(2-amino-pyridinium)-propionate and GIAO/B3LYP/6-31G(d,p) calculated isotropic shielding tensors ($\delta_{\text{exp}} = a + b^*\sigma_{\text{calc}}$) have been obtained.

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References

- [1] X. Domingo, in: E.G. Lomax (Ed.), Amphoteric Surfactants, Marcel Dekker, New York, 1966, pp. 75–190.
- [2] E. Alcalde, M. Gisbert, L. Perez-Garcia, Chem. Pharm. Bull. 44 (1996) 29; E. Alcalde, M. Gisbert, L. Perez-Garcia, I. Dinares, J. Frigola, J. Org. Chem. 56 (1991) 6516; E. Alcalde, I. Dinares, J. Frigola, C. Jaime, J.-P. Fayet, M.-C. Vertut, C. Miravittles, J. Rins, J. Org. Chem. 56 (1991) 4223 (and references cited therein).
- [3] M. Szafran, Z. Dega-Szafran, A. Katrusiak, G. Buczak, T. Głowiąk, J. Sitkowski, L. Stefaniak, J. Org. Chem. 63 (1998) 2898.
- [4] M. Szafran, J. Koput, J. Baran, T. Głowiąk, J. Mol. Struct. 436–437 (1997) 123.
- [5] Z. Pajak, P. Czarnecki, H. Muszyńska, B. Szafranka, M. Szafran, J. Chem. Phys. 113 (2000) 848.
- [6] M. Szafran, I. Kowalczyk, A. Katrusiak, Z. Dega-Szafran, J. Mol. Struct. 651–653 (2003) 621.
- [7] M. Szafran, A. Katrusiak, I. Kowalczyk, Z. Dega-Szafran, J. Mol. Struct. 657 (2003) 125.
- [8] Z. Dega-Szafran, M. Jaskólski, M. Szafran, J. Mol. Struct. 555 (2000) 191.
- [9] M. Szafran, Z. Dega-Szafran, G. Buczak, A. Katrusiak, M.J. Potrzebowski, A. Komasa, J. Mol. Struct. 416 (1997) 145.
- [10] X.-M. Chen, T.C.W. Mak, J. Mol. Struct. 221 (1990) 256.
- [11] Z. Dega-Szafran, M. Grundwald-Wyspiańska, I. Kowalczyk, M. Szafran, J. Mol. Struct. 322 (1994) 297.
- [12] J. Baran, Z. Dega-Szafran, M. Jaskólski, M.K. Marchewka, H. Ratajczak, M. Szafran, J. Mol. Struct. 406 (1997) 127.
- [13] M. Szafran, A. Katrusiak, Z. Dega-Szafran, M. Drozd, J. Mol. Struct. 689 (2004) 213.

- [14] G. Buczak, Z. Dega-Szafran, A. Katrusiak, M. Szafran, *J. Mol. Struct.* 436–437 (1997) 143.
- [15] X.-M. Chen, T.C.W. Mak, *Acta Crystallogr. C*50 (1994) 1807.
- [16] Z. Dega-Szafran, A. Katrusiak, M. Szafran, *J. Mol. Struct.* 555 (2000) 203.
- [17] M. Szafran, M. Jaskólski, I. Kowalczyk, Z. Dega-Szafran, *J. Mol. Struct.* 448 (1998) 77.
- [18] Z. Dega-Szafran, A. Katrusiak, M. Szafran, *J. Mol. Struct.* 513 (1999) 15.
- [19] Z. Dega-Szafran, A. Katrusiak, M. Szafran, *J. Mol. Struct.* 570 (2001) 165.
- [20] Z. Dega-Szafran, A. Katrusiak, M. Szafran, *J. Mol. Struct.* 610 (2002) 229.
- [21] X.-M. Chen, T.C.W. Mak, *J. Mol. Struct.* 249 (1991) 135.
- [22] P.R. Wei, T.C.W. Mak, *J. Chem. Crystallogr.* 26 (1996) 133.
- [23] H. Zhao, L.-H. Huo, S. Gao, Z.-Y. Zhang, J.-G. Zhao, S.W. Ng, *Acta Crystallogr. E*60 (2004) o1501.
- [24] W.B. Rybakov, S.G. Zukov, E.V. Babayev, O.S. Mazina, L.A. Aslanov, *Kristalografija* 44 (1999) 1067.
- [25] M. Szafran, I. Kowalczyk, J. Koput, A. Katrusiak, *J. Mol. Struct.* 744–747 (2005) 59.
- [26] T. Kolev, D. Yancheva, B. Shivachev, R. Petrova, M. Spitteller, *Acta Crystallogr. C*61 (2005) o213 (and references cited therein).
- [27] T. Kolev, R. Wartmann, M. Spitteller, W.S. Sheldrick, H. Mayer-Figge, *Acta Crystallogr. E*61 (2005) o1090.
- [28] M. Szafran, I. Kowalczyk, J. Koput, *J. Mol. Struct.* 754 (2005) 85.
- [29] G.M. Sheldrick, *SHELXS-97*, Program for Solution Crystal Structure, University of Göttingen, 1997.
- [30] G.M. Sheldrick, *SHELXL—97*, Program for Solution Crystal Structure Refinement, University of Göttingen, 1997.
- [31] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, A.J. Jr. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, *GAUSSIAN98*, Revision A 6, Gaussian, Inc., Pittsburg, PA, 1998.
- [32] A.D. Becke, *J. Chem. Phys.* 98 (1994) 5648.
- [33] P.J. Stephenson, F.J. Devlin, C.F. Chabalewski, M.J. Frisch, *J. Phys. Chem.* 98 (1994) 11623.
- [34] W.J. Hehre, L. Random, P.V.R. Schleyer, J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1989.
- [35] A. Kvick, J. Noordik, *Acta Crystallogr. B*33 (1977) 2862.
- [36] K. Wijaya, O. Moers, P.G. Jones, A. Blaschette, *Acta Crystallogr. C*57 (2001) 167.
- [37] E. Pretsch, P. Buhlman, C. Affolter, *Structure Determination of Organic Compounds Tables of Spectral Data*, Springer, Berlin, 2000.
- [38] H.I. Abdulla, M.F. El-Bermani, *Spectrochim. Acta A* 57 (2001) 2659.
- [39] Y. Buyukmurat, S. Akyuz, *J. Mol. Struct.* 651–653 (2003) 533.
- [40] M. Szafran, J. Koput, *J. Mol. Struct.* 381 (1996) 157.
- [41] K.M. Harmon, G.F. Avci, *J. Mol. Struct.* 117 (1984) 295.
- [42] M. Viertorinne, J. Valkonen, I. Pitkänen, M. Mathlouthi, J. Nurmi, *J. Mol. Struct.* 477 (1999) 23.
- [43] K. Wolinski, J.F. Hinton, P. Pulay, *J. Am. Chem. Soc.* 112 (1990) 8251.
- [44] M. Häser, R. Ahlriches, H.P. Baron, P. Weiss, H. Horn, *Theor. Chim. Acta* 83 (1992) 455.
- [45] M. Bartfield, P. Fagerness, *J. Am. Chem. Soc.* 119 (1997) 8699.
- [46] Z. Dega-Szafran, M. Szafran, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* 43 (1995) 295.
- [47] X.-M. Chen, T.C.W. Mak, *J. Chem. Soc. Dalton Trans.* (1991) 3252.
- [48] X.-M. Chen, T.C.W. Mak, *J. Mol. Struct.* 245 (1991) 301.